

D. M. Fanning and I. K. Robinson (U. of Illinois, UC)

Superstructure reflections of a single crystal (2 mm per side) of lead magnesium niobate ($\text{Pb}[\text{Mg}_{1/3}\text{Nb}_{2/3}]\text{O}_3$) were studied at beamline X16C. PMN is a ferroelectric relaxor with a Curie temperature of -7 °C. It has a broad, frequency dependent transition to the ferroelectric state. PMN's structure is perovskite with the mixed B-site containing a Mg^{2+} or Nb^{5+} ion.

Integrated intensities were measured for about 80 reflections by scanning in the hkl directions. The width of each superstructure reflection was roughly constant and indicative of an ordered domain size of 20 Å from the Scherrer equation:

$$L = 2\pi \cdot 0.94 / \Delta q_{FWHM}$$

The crystal was carefully mounted so that the beam entered and exited through the same face. In this way, the absorption correction was simply $1/(\sin\theta\sin\chi)$. However, this correction is important as it critically affects the form of the data.

The corrected structure factors as a function of momentum transfer are plotted in Figure 1. The shape of the data suggests that chemical ordering is the cause of PMN's superstructure reflections. In a chemically ordered sample, the structure factors are simply proportional to the difference in the ordered chemicals' form factors. Without the absorption correction, the data increase at first with q and then decrease. This would suggest a displacement ordering model.

The fit to the data in Figure 1 represents our proposed model. We assumed one-to-one Mg:Nb chemical ordering within PMN's ordered regions and allowed the oxygen ions to displace towards or away from the B-sites (Figure 2). The best fit was found with an oxygen displacement of 0.1 Å towards the smaller Nb^{5+} ion and away from the Mg^{2+} ions. The Pb ions are believed to be randomly displaced about their ideal position, and we were unable to improve our fit by displacing those ions.

PMN is unique in that its ratio of different B-site ions (Mg:Nb) is 1:2, yet it chemically orders in a 1:1 ratio. Of course, the charge imbalance greatly restricts the size of these ordered domains. In future experiments, we plan to look at La-doped PMN crystals in which the La^{3+} ions provide an extra positive charge compared to the Pb^{2+} ions. This reduces the charge imbalance in the ordered domains, allowing them to grow larger.

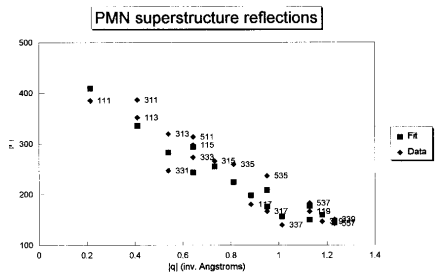


Figure 1. Structure factors of the type $(h+1/2, k+1/2, l+1/2)$ v. momentum transfer.

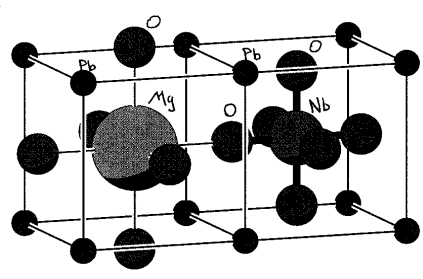


Figure 2. Ordered Mg and Nb ions in adjacent unit cells.